DETERMINATION OF TOTAL ORGANIC EMISSIONS FROM HAZARDOUS WASTE COMBUSTORS

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ABSTRACT

U.S. Environmental Protection Agency risk assessment guidance currently under development for evaluation of permitting information from hazardous waste combustors requires a quantity referred to as "Total Organic Carbon." The risk guidance does not define this term precisely, nor does it explain how it should be determined. This paper discusses basic principles of sampling and analysis of stack emissions for "Total Organics," best currently available technology, and the status of two ongoing projects designed to provide guidance and to improve analysis procedures.

Determination of "Total Organics " from stack emissions is much more complicated than might be expected, and more published guidance is badly needed. The best scheme available for analysis of stack emissions for "Total Organics" to be used in material balance style "bookkeeping" includes determination of organics content in three boiling point ranges; less than 100°C, 100°C to 300°C, and greater than 300°C. Total organic carbon (TOC) is not a useful quantity, since it includes soot, polymeric material, and other non-extractable organic materials. "Total Organics" has been found to be an imperfect, but less misleading term. Various calculations can be made and conclusions can be drawn based on the contents of the individual boiling point ranges, as determined by the recommended methodology. The analysis strategy is complicated, difficult, and contains limitations and compromises. It does not, however, require exotic analysis instrumentation, nor is it very expensive. Each of these facets of the methodology is discussed in the paper, along with a status report on development of a guidance document and a research project intended to produce improved methods.

INTRODUCTION

Characterization of stationary source stack emissions is difficult and expensive, at best, but problems increase exponentially as the required thoroughness of analysis increases. A survey analysis which accounts for a high percentage of the organic compounds present in the emissions is very difficult to achieve in all but the most exceptional cases. This is particularly true when combustion sources are involved, since the normal mixture of products of incomplete combustion is much more complex than emissions from a simple source such as a dry cleaning plant. Sampling and analysis for a designated list of pollutants is always much simpler than performing a reasonably complete characterization of all the components of the emissions. Answering the question, "What is there?" is always more difficult than answering the question, "Is compound x there?". In the past, hazardous waste combustor emissions sampling and analysis for permitting and other regulatory activity was primarily concerned with a relatively short list of performance indicator compounds designated as Principal Organic Hazardous Constituents (POHCs). Only a limited number of research projects were carried out for the purpose of approaching a complete characterization of products of incomplete combustion and other organic compounds (1). Today, a much greater use of risk assessment as a permitting and general regulatory tool increases the need for comprehensive characterization of emissions. A key element in carrying out a thorough characterization of waste combustor emissions is determination of the amount of total organic material in the emissions in order that the percentage of uncharacterized emissions may be tracked. Other benefits and uses of this quantity will be discussed below.

Risk assessment guidance (2), currently under development by the U.S. Environmental Protection Agency's Office of Solid Waste, for evaluation of permitting information from hazardous waste combustors requires a quantity referred to as "Total Organic Carbon." The risk assessment guidance does not define this quantity precisely, nor does it explain how it should be determined. It is anticipated that the final version of the risk assessment guidance will call the required quantity "Total Organics." This paper discusses basic principles of sampling and analysis of stack emissions for "Total Organics," best currently available technology and status of projects to provide guidance and to improve analysis procedures.

CONCEPTS AND STRATEGIES

A previous publication (3) discussed screening survey strategies for organic compounds in hazardous waste combustor emissions. Several concepts were introduced which had evolved from earlier research cited therein. The idea was introduced of using "Total Organics" as part of a chemical "accounting" system for estimation of percent completeness of analysis. The concept of an iterative analysis scheme was discussed where the number of passes through the analysis and decision loop depended upon information gained versus goals of the project. A risk-driven analysis strategy was suggested which utilized the other concepts in a material balance manner, and further utilized the "Total Organics" to estimate risk from unidentified organic compounds. Estimation of completeness of analytical characterization and risk from unidentified organic compounds are both benefits that make the use of the "Total Organics" concept attractive to those implementing risk assessment technologies.

In dealing with any system for sampling or analysis or in utilizing data from such a system, it is always crucial to understand the strengths, weaknesses, and inherent limitations of the methodology. Nowhere is this principle more true than with respect to "Total Organics" analysis. The first rule to understand is that any analytical method title that begins with "Total" is almost always inaccurate. Organic compounds can usually be analyzed individually more accurately, precisely, and unambiguously than in groups. Analytical chemists create methods for groups of compounds in order to fill a scientific need, a regulatory need, or sometimes in an attempt to save on analysis costs. All three are sound reasons for developing group methods, and no harm is done unless users misunderstand limitations of data from the methods. A descriptive title is usually given to an analysis method to make it easier to remember and to give the unfamiliar reader a clue as to what the method measures. Unfortunately, such names as "total hydrocarbons," "total organic carbon," and "total halogenated organics" are often ambiguous or misleading. "Total Organics" is less misleading than some alternative terminology, but is certainly far from perfect. Knowledge of the methods is the only effective defense against being misled. One of the major goals of this paper is to make knowledge of the "Total Organics" methodology more widely available.

Any analytical method is only useful to the extent that the data produced by its application provide information relevant to the questions under consideration by the investigator or regulator. The "Total Organics" method, therefore, must provide data that can be used for estimation of completeness of analytical characterization and for estimation of risk from the unidentified residual organic material. The methodology initially appears to be very simple, but rapidly becomes complicated when practical problems of implementation are considered. As described below, a number of strategical and tactical decisions have been made in order to make the method produce data applicable to the intended end use. Each of those choices results in certain benefits to the method, but also brings with it a burden of limitations and liabilities. Even though the procedures to be described contain many compromises and are certainly not a model of perfection, they have been thoroughly thought out and are backed by a certain amount of laboratory research. The analytical procedures are also relatively inexpensive to implement, and do not require exotic equipment.

One of the first decisions that must be made in planning a strategy for sampling and analysis of "Total Organics," is what exactly is meant by "Total." It must be decided how much can and should be included so as to optimize usefulness of the data without exceeding the bounds of practicality and affordability. "Total Organics," in the method about to be described, means the total amount of organic material which is recoverable by means of solvent extraction or other preparatory steps used in the survey analysis. This quantity can be used as a standard against which to measure percent completeness of analysis, as well as an estimation factor for risk calculations.

In its present form, the "Total Organics" strategy requires a separate set of samples in addition to those taken for comprehensive analysis. Samples taken by Method 0010 and by Draft Method 0040 are sufficient to include most of the organic compounds found in hazardous waste combustor emissions (4,5). Three analytical procedures, which will be described in more detail later, are the minimum set of operations required to produce "Total Organics" as defined above. The three procedures are named Field GC (FGC), Total Chromatographable Organics (TCO), and Gravimetric Analysis (GRAV).

A few words are necessary about why certain other organic analysis techniques are inappropriate for the current application. Total Organic Carbon (TOC) analysis is often used to obtain an estimate of the organic content of water and wastewater samples. Methods 9060 and 9060a (6,7) are examples of this approach to total organic analysis. The basic strategy is to convert the organics to carbon dioxide, which is then detected directly or after further conversion to methane. Many variations of this procedure are discussed in Reference 8. TOC analysis is not suitable for application to many combustion samples. If applied directly to particulate material, it would include carbon from soot, polymeric material, and other generally non-extractable organic materials. Since these non-recoverable materials are not likely to be toxic and will definitely not appear on the characterized side of the compound material balance, they are best excluded from further consideration. The use of TOC in the "Total Organics" scheme is further prohibited because it cannot be used to determine the organic content of an extract without interference from the solvent used for extraction of the samples. Method 25, for volatile organic compound analysis employs conversion of carbon to carbon dioxide followed by conversion to methane and detection in that form (9). Method 25 has detection limit and interference problems and measures an ill-defined collection of compounds, thus making it unsuitable for use in the "Total Organics" methodology.

RECOMMENDED METHODOLOGY

A brief summary of the current methodology will be given here. Two ongoing projects to provide detailed guidance and improvements in the technology will be discussed in a later section. The scheme described here is the result of dozens of critical decisions, some made 17 years ago and others within the last month. It is strongly believed to be the best currently available procedure for generating a "Total Organics" analysis for the purposes previously discussed. Reasons for selection of these particular methods are discussed in the next section. The sampling and analysis procedures described are the minimum required for adequate performance. In some situations, supplementing the scheme with <u>additional</u> sampling or analysis procedures might be beneficial. Substitution of methods for the core scheme is not recommended.

Analysis of the samples is carried out in three categories, which were introduced previously. The three compound categories, each corresponding to a boiling point range, have descriptive names intended to be unique within the environmental analysis field and to have as little potential for misleading interpretation as possible. The FGC category includes compounds with boiling points less than 100°C, TCO contains compounds boiling over the range 100°C-300°C, and GRAV represents organics boiling above 300°C.

Likewise, the specified sampling methods effectively collect organic compounds boiling over a fairly well defined range, and are not quantitative for materials outside that range. As previously mentioned, samples for "Total Organics" analysis are collected using Draft Method 0040 and Method 0010. Samples from Draft Method 0040 are subjected to FGC analysis, while those from Method 0010 are analyzed for TCO and GRAV. Draft Method 0040 employs a Tedlar® bag to collect volatile organics. Sampling is integrated over a one or two hour time period in order to match the normal collection time of the other stack sampling methods. The probe and sampling lines are maintained in the temperature range of 130°C-140°C to minimize sorption related sample losses. As the name implies, Field GC analysis is carried out at or very near the sampling site. On-site analysis, usually within a hour after sample collection, minimizes sample loss due to storage and shipping. The analysis is by gas chromatography with flame ionization detection (GC-FID), and results are reported in seven subcategories according to boiling point range. This subcategory analysis and reporting procedure, in contrast to reporting total FGC results, produces data containing additional information which may be invaluable during the interpretation phase. It is strongly recommended that methane be determined as an individual compound during the FGC analysis. Methane is usually a major component of the volatile organic emissions from a hazardous waste combustor, and it is beneficial having its mass in the assigned side of the material balance rather than as a part of the unidentified component when the "Total Organics" data is used for interpretation of survey analysis results.

The TCO and GRAV analyses are performed on samples collected by Method 0010. The sampling train in Method 0010 is also known as the Modified Method 5 Train (MM5) or the Semivolatile Organic Sampling Train (Semi-VOST). This sampling method is the most nearly universal of those available, in that it performs adequately on the largest assortment of organic compounds and operates under the widest variety of adverse conditions and potentially interfering materials and situations. Organic compounds are recovered from the various components of the sampling train according to Draft Method 3542 (10). The resulting three dichloromethane extracts from the MM5 train are combined before analysis for TCO and GRAV. TCO analysis is a form of low resolution GC-FID, where the area under the response curve is integrated between boiling points 100°C and 300°C. GRAV analysis is accomplished by carefully evaporating the extract to dryness and weighing the residue. Although the central concept in GRAV analysis is very simple, successful execution requires a great deal of skill and careful work. Any inattention to the samples or lack of good laboratory technique will result in either contamination or loss of samples, especially during the extract concentration and drying steps. "Total Organics" is obtained by adding $\mu g/m^3$ of FGC, TCO and GRAV. The individual boiling point category and subcategory data should also be reported, since this information may be very useful during later interpretation. For example, unidentified mass in the GRAV range cannot be due to vinyl chloride, just as unidentified material in the FGC analysis cannot be dioxin or polycyclic aromatic hydrocarbons.

EVOLUTION OF THE METHODOLOGY

Much of the fundamental methods technology for "Total Organics" was developed in the late 1970s and early 1980s as part of an EPA program designed to assess and prioritize potential environmental impact of emissions from a wide range of energy-related and industrial sources (11,12,13). Strategies and many of the methods have evolved since that time, but the fundamental principles involved have remained the same.

Weighing is the most nearly ideal method of detecting total organics. All of the other detection systems suffer from compound-specific response factor variations. These variations can be compensated for by calibration when analyzing for any given list of compounds. When attempting to quantitate organic material of unknown species, calibration with individual compounds introduces error of an indeterminate magnitude. It also is logical that a weight determination is appropriate since the"Total Organics" quantity is ultimately to be compared with and related to other data in the form of $\mu g/m^3$ of specific compounds. In spite of being a nearly ideal detection method, weighing the organic material does have two troublesome limitations. Sensitivity can be a problem when small amounts of material are involved, and the need to physically separate the organic compounds of interest from a solid or solvent matrix places additional demands on the analytical scheme.

It was understood initially that the relatively straightforward approach of evaporation of dichloromethane extracts to dryness followed by weighing would result in loss of the more volatile compounds. Consultation with approximately a dozen respected analytical chemists produced agreement that compounds with boiling points below approximately 100°C would be lost, but that higher boiling compounds would be quantitatively retained. That unanimous estimate was eventually proven incorrect, but early strategy development was based upon it and supplemented later. It was obviously necessary that the GRAV analysis be supplemented to offer coverage of the lower boiling compounds. In addition to expecting loss of the low boilers during GRAV analysis, it was known that compounds boiling below 100°C would not be collected quantitatively with the MM5 train. It was therefore necessary to add a sampling method to the evolving "Total Organics" scheme along with an analytical procedure. Glass bulb grab samplers were chosen over sorbent samplers because of their ability to collect gaseous compounds such as methane and their ability to deal with higher concentration ranges. Glass bulbs were chosen over plastic sampling bags because of better sample storage characteristics (14).

Weighing the low boiling organics was not considered feasible because of the weight discrepancy between the container and the contents, because of the requirement to separate the organics from inorganics, and because it was necessary to be able to discriminate the organic compounds boiling below 100°C from those boiling above 100°C. Failure to make the latter delineation could have resulted in counting the mass of some of the compounds twice. Conversion of the organics to CO_2 or CH_4 before sensing, as in TOC analysis or Method 25, would have caused loss of the ability to isolate the compounds with boiling points <100°C and would also have created a method subject to interference from CO_2. The ability of gas chromatography (GC) to separate both organics and inorganics as well as its ability to discriminate compounds by boiling point made it an easy choice for the separation method. The choice of detector to use with the GC was not quite as easy. The final choice was made between FID and Mass Spectrometry (MS). Both are nearly universal detectors with unit response factors for many compounds. The FID was selected because of lower cost, better field ruggedness and portability, and unit response for a higher proportion of organic compounds. Even though the consistency of response of the FID to different compounds is better than that of MS, it is still not perfect by any means. It generally acts as a carbon counter, but has lower response for halide-substituted compounds, oxygenated materials, and certain other compounds. At the time the FID was selected as the detector for the FGC system, this reduced response for a relatively small fraction of the compounds likely to be encountered was considered a reasonable compromise. Possible implications with respect to waste combustor emissions will be discussed in a later section.

The biggest change to the FGC method was made recently because of its evolving use in material balance types of calculations. Even though the glass sampling bulbs have better long term sample storage characteristics, grab samples may not correspond well with integrated samples collected over a one to two hour time period. Accordingly the integrated bag, Draft Method 0040, has replaced the glass bulb grab sampler. In addition, Draft Method 0040 has provisions for heated probe and sample lines, as well as the ability to tolerate reasonably high levels of particulate matter and moisture.

Soon after initial development of the GRAV method, a project was undertaken to evaluate the performance of it and other screening tools. Laboratory studies produced evidence that the GRAV procedure quantitatively recovered only those compounds boiling above 300°C rather than the expected 100°C (15). It was apparent that a third analytical method must be added to the "Total Organics" methodology in order that the compounds in the 100°C-300°C boiling point range be counted. No additional sampling method was needed, since the extract from the MM5 train contained the compounds of interest. The solution to the problem was to apply an extension of FGC analysis technology to an aliquot of the Method 0010 extract. The extract aliquot is subjected to GC analysis with detection by FID and integration of the area under the response curve between boiling points 100°C and 300°C. This is the TCO procedure introduced in a previous section.

LIMITATIONS OF THE METHODOLOGY

This paper can certainly not discuss all of the limitations of the recommended methodology, but several of the more important ones will be examined. The reader should keep in mind that these are limitations of the <u>best</u> technology. The alternative methods all have more severe shortcomings. One of the more outstanding problems is the reduced response of the FID to oxygenated and especially to halogenated compounds. Because many of the hazardous materials destroyed by combustion are chlorinated, this limitation is potentially more troublesome in the current application than it was when the scheme was devised. One possible solution is to supplement the FGC and TCO components of the scheme with detectors in addition to the FID. One detector which has shown potential for unit response from chlorinated organic compounds is the Catalytic Flame Ionization Detector (CFID) (16). Research may show that this detector can be effectively utilized in the "Total Organics" scheme.

Another problem related to "carbon counters" such as FID and CFID are that they give no information about the elemental composition of the individual compounds in the mix. In the absence of such information, one can only assume a formula for the "average compound" of the mix, and report the data as if the mixture was really one compound. No matter how cleverly one chooses this average composition, error is still introduced in proportion to variation from the real formula. Supplementing the FGC and TCO analysis with GC-MS analysis solves the molecular formula problem, but adds to the cost. Ways to use GC-MS more efficiently in the overall strategy are being investigated.

Even though Draft Method 0040 is a big improvement over glass sampling bulbs, it will still introduce anisokinetic sampling errors for water soluble organics if large water droplets are present in the flue gas being sampled. It is no worse in this respect than other methods for volatile organics, so the overall effect may be minimal.

Care must be taken in concentrating the dichloromethane extract for TCO analysis. Several reputable laboratories have reported difficulty with loss of compounds in the 100°C-130°C b.p. range when concentrating for GC-MS analysis. It is to be expected that these laboratories, and perhaps others, must exercise special care if the same losses are to be avoided when performing TCO analysis.

Dichloromethane was chosen as the extraction solvent for the "Total Organics" scheme because it is the best "universal solvent" when all organics are considered, and because its boiling point of 48°C makes it easy to remove by evaporation. Even though dichloromethane is best for most compounds, certain ones extract better into other solvents. Survey analysis schemes sometimes supplement the primary dichloromethane extraction with sequential extractions with toluene or ethers. TCO analysis can be run on these extracts without significant modification. The 300°C GRAV analysis lower boiling point cutoff is no longer defined, however, when the extract has a boiling point other than 48°C.

The current version of the "Total Organics" analysis requires the sample from a separate Method 0010 train. The main reason is that addition of various standards added to the catch from the primary train would register as "Total Organics," and complicate interpretation of results. It is probable that a protocol for subtracting these compounds back out of the results can be devised, but it is not as straightforward as might be imagined.

STATUS OF GUIDANCE AND RESEARCH

This paper is intended to convey the basic theory, historic perspective, and a brief summary of the "Total Organics" methodology. Two other projects related to this analysis scheme are currently being carried out under contract to the U.S. EPA. The goal of the first project is to produce a technical guidance document with sufficient details to allow the reader to carry out the various component analyses of the methodology as they now exist. A first draft of this document has been prepared, and a revised version suitable for peer and policy review is expected during April of 1995. The published document should be available by July of 1995. The second project is intended to conduct research to improve the technology employed by the "Total Organics" scheme and to then modify the technical guidance to take advantage of the improvements. The project will explore the use of alternate or supplementary detectors, efficient use of GC-MS, feasibility of using supercritical fluid extraction technology in the scheme, use of microgravimetric techniques, and other research questions that may arise as the work is carried out. A research report and a second edition guidance document will be completed by September 30, 1995. The second edition guidance document should be published by late November 1995. If the research report is released as an EPA report, it should be published in the same time frame.

All methods that are referred to as "Draft" are currently in the process of being promulgated as parts of the third update to the SW-846 Methods Manual (17). It is expected that the proposed third update package will be published for public comment in May 1995. The guidance document for "Total Organics" will contain copies of the most current versions of the draft methods obtainable at the time of publication. It should be possible to include final versions of all the methods in the second edition of the technical guidance document.

NOTICE

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of trade names or commercial products does not constitute endorsement or recommendation for use.

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